ENHANCED LOW TEMPERATURE PERFPRMANCE OF Li-ION BATTERIES USING NANOPHASE MATERIALS

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ABSTRACT

Future Army Combat and Force Warrior Systems will require novel Li-ion batteries that can operate at higher rates and lower temperatures than the currently available Li-ion batteries. One major problem that limits the rate capability at low temperatures of the current Li-ion batteries is the anode material, graphite. In order to overcome the limitations associated with graphite new anode materials must be developed. One such potential new anode material that could lead to higher rates at the low temperatures required by the Future Army Combat and Force Warrior Systems is $Li_4Ti_5O_{12}$ with a nanophase particle size. At present, no information on the rate capability at low temperature of nanophase $Li_4Ti_5O_{12}$ is available. Hence, such information is needed.

Two different nanophase $Li_4Ti_5O_{12}$ particle sizes were investigated, 350 and 700 nm, over the temperature range 20, 0, -10, -20, and -30 ºC at low rates (0.1 C, C=theoretical capacity) to high rates (5C). Electrochemical testing revealed that the 350 nm $Li_4Ti_5O_{12}$ material exhibited higher capacity compared to the 700 nm $Li_4Ti_5O_{12}$ at all rates tested at room temperature and at low rates at low temperatures (<0ºC). This expected behavior is a result of the shorter diffusion lengths and higher number of lithium insertion sites in the smaller particle size material. This result also reveals the importance of reducing the $Li_4Ti_5O_{12}$ particle size as small (i.e., from micron to nano) as possible for enhancing low temperature performance. However, at high rates at low temperatures (<0ºC) a change in behavior was observed, in that the larger particle size $Li_4Ti_5O_{12}$ exhibited the higher capacity. It was observed that as the temperature was decreased the rate at which this transition occurred was also lowered. It is believed that the origin of this transition behavior is that as temperature is lowered the resistance of the $Li_4Ti_5O_{12}$ interparticle contacts increases and controls the discharge rate. This result was unexpected and suggests that at low temperatures and high rates just reducing the $Li_4Ti_5O_{12}$ particle size to the nanoscale is not enough to enhance low temperature performance.

1. INTRODUCTION

Future Army Combat and Force Warrior Systems will require novel Li-ion batteries that can operate at higher rates and lower temperatures than the currently available Li-ion batteries. One major problem that limits the rate capability at low temperatures of the current Li-ion batteries is the anode material, graphite. In order to overcome the limitations associated with graphite new anode materials must be developed. One such potential new anode material that could lead to higher rates at the low temperatures required by the Future Army Combat and Force Warrior Systems is $Li_4Ti_5O_{12}$ with a nanophase particle size. $Li_4Ti_5O_{12}$ with a micron particle size offers the advantages of higher recharge rate at room temperature compared to graphite because its operating voltage is ~ 1.5 Volts versus lithium, which results in no lithium deposition during recharging or film formation on particle surfaces as result of solvent decomposition. (Colbow et al., 1989; Ferg et al., 1994). However, it is well known that there is a dramatic reduction in the rate capability of electrode materials as temperature is reduced (Huang et. al., 2000; Sides and Martin, 2005). One solution to overcome this problem is through the use of nanophase materials. Nanophase materials offer the advantage of enhanced rate at low temperature as a result of their reduced diffusion lengths and increased surface area compared to micron size materials. Thus, it would be expected that nanophase $Li_4Ti_5O_{12}$ may exhibit the rate capability at the low temperatures that the Future Army Combat and Force Warrior Systems will be require. At present no information on the rate capability at low temperature of nanophase $Li_4Ti_5O_{12}$ is available. Hence, such information is needed.

It is the purpose of this paper to present the first results on the rate capability at low temperature of nanophase $Li_4Ti_5O_{12}$. We will report on the low temperature performance of nanophase $Li_4Ti_5O_{12}$ as a function of particle size and rate.

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2. EXPERIMENTAL

2.1. Processing

Two different particle size nanophase $Li_4Ti_5O_{12}$ samples were compared: 1] Nanomyte™ $Li_4Ti_5O_{12}$, obtained from NEI corporation, hereafter referred to as NEI-$Li_4Ti_5O_{12}$ and 2] a larger particle size $Li_4Ti_5O_{12}$ prepared at the Army Research Laboratory (ARL) using a solid-state method, referred to as ARL-$Li_4Ti_5O_{12}$. The ARL material was prepared from TiO_2 (rutile structure) and Li_2CO_3. Three weight percent excess Li_2CO_3 was used to compensate for lithia volatilization during the high temperature heating. The starting materials were ground with an alumina mortar and pestle with enough methanol to form a slurry. The dried and mixed reactant mixture was heated at 800°C for 12 h in air. The sample was reground, pelletized and heated for another 24 h at 800°C in air.

2.2. Characterization

The structure of the $Li_4Ti_5O_{12}$ samples was determined by X-ray diffraction using a Rigaku Ultima III diffractometer with Cu K alpha radiation. Lattice constants were determined by obtaining diffraction data in a parallel beam diffraction geometry and fitting the data using Rietveld refinement. Crystal size was evaluated by collecting diffraction data in a Bragg-Brentano (focusing) geometry and correcting for instrumental broadening by using LaB_6 (NIST; 660A). The particle size of the $Li_4Ti_5O_{12}$ samples was determined using two different techniques. The first method was based on the surface area. Surface area measurements were conducted by the Brunauer-Emmett-Teller (BET) method using N_2 as adsorbate gas. The average particle size diameter was calculated based on this surface area assuming a spherical particle. The second method involved measuring the particle size from scanning (SEM) and/or transmission (TEM) electron photomicrographs.

2.3. Electrochemical Testing

For electrochemical testing, a composite electrode with a load of 2.10±0.05 mg cm^{-2} was fabricated by a slurry coating method. Using γ-butyrolactone as solvent, a slurry of 78 wt.%$Li_4Ti_5O_{12}$, 12wt.% polyvinylidene fluoride and 10 wt. % super-P carbon was prepared and coated onto an aluminum foil substrate. The electrode film was cut into small discs with an area of 0.97 cm^2 and dried at 60° C in air before use. In a dry room (Dew point <-80°C), Li/$Li_4Ti_5O_{12}$ button cells were assembled using Celgard membrane as the separator and a 1.0 M $LiPF_6$ solution in a 1:1 (wt.) mixture of propylene carbonate (PC) and 1,2-dimethoxyethanen (DME) electrolyte. A Tenney Environmental Oven was used to provide constant temperature at 20, 0, -10, -20, and -30 ºC. Cycling

testing was performed using a Maccor Series 4000 tester. The cells were cycled between 3.0 and 1.0 V at C-rates from 0.1 to 5 (where the theoretical capacity of $Li_4Ti_5O_{12}$ is 175 mAh/g, Thackeray, 1995).

3. RESULTS and DISCUSSION

3.1. Material characterization

Figure 1 shows the x-ray diffraction patterns for: A) NEI-$Li_4Ti_5O_{12}$ and B) ARL-$Li_4Ti_5O_{12}$.
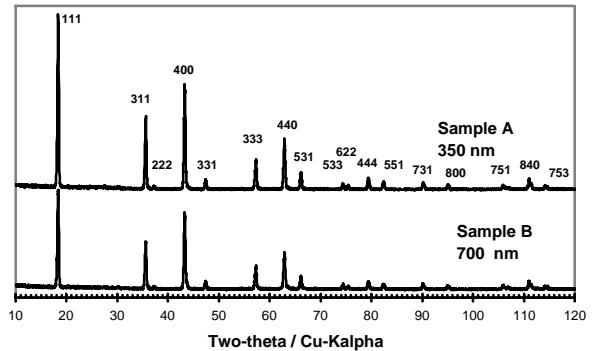
Fig. 1. X-ray diffraction patterns for: A) NEI-$Li_4Ti_5O_{12}$ and B) ARL-$Li_4Ti_5O_{12}$.

From Fig. 1. several important points are noted. Firstly, both patterns are similar. They both can be indexed to a cubic spinel single-phase material with a Fd3m space group. No second phases were observed in either pattern. Secondly, the lattice constants as determined from Rietveld analysis of the XRD patterns are ~8.356 for both ARL-$Li_4Ti_5O_{12}$ and NEI-$Li_4Ti_5O_{12}$. This value is in good agreement with values for $Li_4Ti_5O_{12}$ prepared under an air atmosphere at high temperature (Ohzuku et al., 1995). Thirdly, the average crystal size estimated for NEI-$Li_4Ti_5O_{12}$ from measurement of the broadening of the X-ray reflections using the Scherrer formula (West, 1984) is ~230 nm. The ARL-$Li_4Ti_5O_{12}$ has a crystal size too large to be measured via X-ray reflection line broadening.

BET surface areas of 2.46 and 4.85 m^2/g were measured for ARL-$Li_4Ti_5O_{12}$ and NEI-$Li_4Ti_5O_{12}$, respectively. The average particle size diameter was calculated based on this surface area assuming a spherical particle using the equation below (Kavan et al., 2002):

$$d = 6 / \rho S_{BET} \qquad (1)$$

where d is the particle size, ρ is the density of $Li_4Ti_5O_{12}$ (3.5 g / mL) and S_{BET} is the BET surface area. A particle size of 700 nm was calculated using equation 1 for the

NEI-$Li_4Ti_5O_{12}$ material and 353 nm for the ARL-$Li_4Ti_5O_{12}$ material.

A typical SEM of the ARL-$Li_4Ti_5O_{12}$ material is shown in Fig. 2. The SEM image shows a fairly uniform particle size of about 700 nm. The morphology can be reasonably approximated as equiaxed.
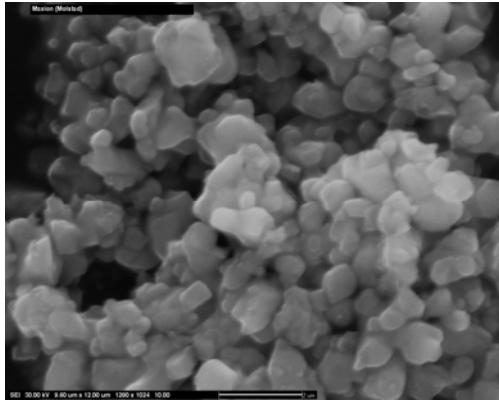

Fig. 2. SEM photomicrograph of ARL-$Li_4Ti_5O_{12}$.
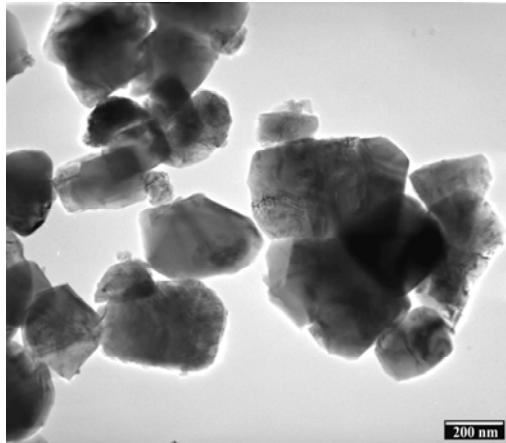
Fig. 3. TEM photomicrograph of NEI-$Li_4Ti_5O_{12}$.

Fig. 3 is a TEM image of NEI $Li_4Ti_5O_{12}$. The TEM image of NEI-$Li_4Ti_5O_{12}$ material shows equiaxed particles of about 350 nm diameter. A summary of the crystal/particle size for the ARL-$Li_4Ti_5O_{12}$ and NEI-$Li_4Ti_5O_{12}$ materials determined by the various techniques; X-ray diffraction, BET and electron microscopy are listed in Table 1. From Table 1 several important points are noted. Firstly, there is excellent agreement for particle sizes determined by BET and electron microscopy. Secondly, the particle size of the ARL-$Li_4Ti_5O_{12}$ material is ~700 nm whereas the particle size of the NEI-$Li_4Ti_5O_{12}$ material is about half the size ~350 nm.

Table 1: Particle Size Characterization

Method	ARL-$Li_4Ti_5O_{12}$	NEI-$Li_4Ti_5O_{12}$
XRD	N/A	~230 nm (crystal size)
SEM	~700 nm	N/A
TEM	N/A	~350 nm
BET	~700 nm	~353 nm

In summary, we can say that both the ARL-$Li_4Ti_5O_{12}$ and NEI-$Li_4Ti_5O_{12}$ materials are single phase spinel, with the ARL-$Li_4Ti_5O_{12}$ material having a particle size of ~700 nm and the NEI-$Li_4Ti_5O_{12}$ material having a particle size of ~350 nm. As a result of the difference in particle size a difference in the low temperature performance of the two materials is expected.

3.2. Electrochemical characterization

3.2.1. Effect of particle size on capacity at low temperature

The first thing that was investigated was the effect of particle size on discharge capacity as the temperature is lowered from room temperature to -30°C. Figure 4 compares the capacity of the NEI-$Li_4Ti_5O_{12}$ (solid line) and ARL-$Li_4Ti_5O_{12}$ (dashed line) materials at room temperature at low rate (rate ≈ C/8). The ARL-$Li_4Ti_5O_{12}$ material had a specific capacity of 163 mAh/g, while the NEI-$Li_4Ti_5O_{12}$ material had a specific capacity of 152 mAh/g. Both materials exhibited discharge capacities near 90% of the theoretical capacity (175 mAh/g) at 23ºC. The slight difference in baseline capacity may result from the fact that the electrode film processing method was developed for micrometer sized materials and may need to be adjusted to account for the use of smaller particles. The voltage of discharge for both samples is 1.5 V, indicating no difference in polarization and in agreement with literature values for the insertion of lithium into $Li_4Ti_5O_{12}$ (Thackeray, 1995). It is important to note that at room temperature at low rates that the reducing the particle size from 700 to 350 nm has no effect on the discharge capacity.
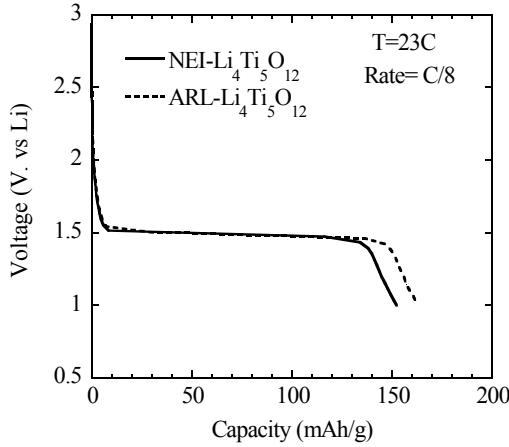
Fig. 4. Discharge curves of ARL-Li$_4$Ti$_5$O$_{12}$ (dashed) and NEI-Li$_4$Ti$_5$O$_{12}$ (solid) at 23°C.

However, when the temperature was lowered a difference in the discharge capacity is observed between NEI-Li$_4$Ti$_5$O$_{12}$ and ARL-Li$_4$Ti$_5$O$_{12}$. When the temperature was lowered to 0° C, the specific capacity of NEI-Li$_4$Ti$_5$O$_{12}$ was 148 mAh/g,, representing a 3% drop in capacity, whereas the capacity of ARL-Li$_4$Ti$_5$O$_{12}$ dropped to133 mAh/g, an 18% drop in capacity. This demonstrates the effect of particle size on capacity as temperature is lowered. This effect is more evident as temperature is further lowered, as shown in Fig. 5. Fig. 5 compares the discharge capacity of NEI-Li$_4$Ti$_5$O$_{12}$ and ARL-Li$_4$Ti$_5$O$_{12}$ at -30°C, the lowest temperature tested.
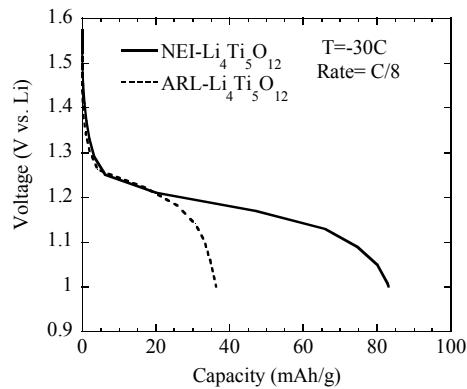
Fig. 5. Discharge curves of ARL-Li$_4$Ti$_5$O$_{12}$ (dashed) and NEI-Li$_4$Ti$_5$O$_{12}$ (solid) at -30°C.

From Fig. 5 it can be observed that the NEI-Li$_4$Ti$_5$O$_{12}$ is still delivering more than 83 mAh/g (47% of the

theoretical capacity) whereas the larger particle size ARL-Li$_4$Ti$_5$O$_{12}$ only delivers 36 mAh/g (21% of the theoretical capacity). This difference is most likely a result that the smaller particle size material has shortened diffusion lengths and increased number of lithium insertion sites, that result from the increased surface area, compared to the larger diameter particle, leading to a higher discharge capacity. The result that higher Li$_4$Ti$_5$O$_{12}$ capacity is exhibited with decreasing particle size, as temperature is lowered, is in agreement with results of Huang et al. (2000) on coke and Slides and Martin (20005) on V$_2$O$_5$ nanorods at low rates.

3.2.2. Effect of rate on capacity at low temperature

The data shown in Fig. 5 is for low rates, typical of equilibrium conditions. What happens at low temperature when the rate is increased to those used in practical applications? It was observed at room temperature that the NEI-Li$_4$Ti$_5$O$_{12}$ material with smaller particle size has higher capacity at all rates tested (from C/8 to 5C). However, as the temperature is reduced it was observed when the rate is increased; there is a cross-over rate at which the ARL-Li$_4$Ti$_5$O$_{12}$ with the larger particle size has higher capacity than the NEI-Li$_4$Ti$_5$O$_{12}$ material with a smaller particle. An example of this behavior is shown in Fig. 6. Figure 6 is a plot of discharge capacity of ARL-Li$_4$Ti$_5$O$_{12}$ (dashed) and NEI-Li$_4$Ti$_5$O$_{12}$ (solid) at -10°C as a function of rate (C/8 to 5C).
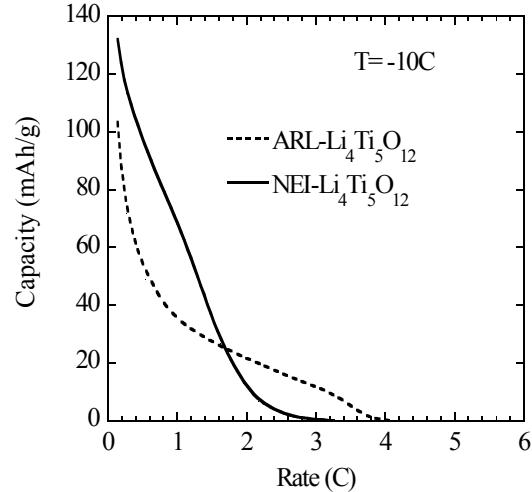
Fig. 6. The discharge capacity of ARL-Li$_4$Ti$_5$O$_{12}$ (dashed) and NEI-Li$_4$Ti$_5$O$_{12}$ (solid) at -10°C as a function of rate.

From Fig. 6 it can be observed that at rates below 1.7C, the NEI-$Li_4Ti_5O_{12}$ (solid) material with a 350 nm particle size has higher capacity but above 1.7C, the ARL-$Li_4Ti_5O_{12}$ (dashed) material with a 700 nm particle size has higher capacity. At rates above 4C the capacity for both materials is close to zero. The cross-over rate (transition rate) as function of temperature is listed in Table 2.

Table 2: Transition rate as a function of temperature

Testing Temperature (°C)	Transition Rate (C)
23	NA
0	3
-10	1.7
-20	1
-30	0.4

From Table 2 it can be observed that as temperature is decreased the transition rate at which the material with larger particle size has the highest capacity is decreased. For example, at 0°C the smaller particle size NEI-$Li_4Ti_5O_{12}$ has higher capacity than ARL-$Li_4Ti_5O_{12}$ up to rates of 3C, whereas at -30°C NEI-$Li_4Ti_5O_{12}$ has the higher capacity up to only rates of 0.4C.

At present, reasons for this transition are uncertain. We can speculate on the reasons for the transition by 1) considering what is different between NEI-$Li_4Ti_5O_{12}$ and ARL-$Li_4Ti_5O_{12}$, 2) considering the effects of the differences and 3) determining, based on the effects, if the difference leads to a plausible explanation. The first difference we consider is surface area. The NEI-$Li_4Ti_5O_{12}$ has approximately two times the surface area of ARL-$Li_4Ti_5O_{12}$. This property will not change as temperature is lowered and, in fact, should lead to better low temperature high rate performance for NEI-$Li_4Ti_5O_{12}$ since the number of insertion sites is directly proportional to the surface area. Therefore, this difference can be excluded as a reason for the transition.

The second difference we consider is particle diameter: NEI-$Li_4Ti_5O_{12}$ has a particle diameter half that of ARL-$Li_4Ti_5O_{12}$. This difference means that the lithium ion diffusion lengths will be shorter for the NEI material and should improve low temperature-high rate performance. Thus, we can also exclude this difference as a reason for the transition.

Third, we can consider the different methods of synthesis: the NEI-$Li_4Ti_5O_{12}$ was made at a lower temperature and therefore one might speculate that there exists a greater possibility that because of the low temperature of synthesis some amorphous or other non-equilibrium phase is present. The ARL-$Li_4Ti_5O_{12}$, synthesized at a higher temperature, is more likely to be fully reacted and contain only the thermodynamically most stable phase, which is presumably $Li_4Ti_5O_{12}$. This possible difference in the two samples may have some effect on the low temperature high rate performance but it is not readily apparent how this would change the low temperature-high rate performance and there is no evidence to support the presence of such a phase or amorphous component. One could also speculate that the differences in synthesis may affect the surface chemistry. But again, it is not readily apparent how this would affect the low temperature high rate performance and we have no evidence of differences in the surface chemistry. Elucidation of possible differences would require considerable experimental work beyond the scope of this paper. Thus, we will conclude that the difference in synthesis may have some effect but we will reasonably conclude that it is probably not the reason for the transition.

Finally, we consider the effect of $Li_4Ti_5O_{12}$ inter-particle contacts. Owing to the fact that the NEI-$Li_4Ti_5O_{12}$ is approximately half the diameter of ARL-$Li_4Ti_5O_{12}$ there will be a proportional increase in the number of inter-particle contacts for a given volume of NEI-$Li_4Ti_5O_{12}$ versus ARL-$Li_4Ti_5O_{12}$. During charge and discharge, electrons are transferred from particle to particle. Each transfer of electrons has a resistivity associated with this process. The effect of introducing interparticle contacts causes an increase in the overall resistance because of the increased number of interparticle contacts, each of which has its own resistance. Could this be part of the explanation for the transition? Well, resistance is a property which varies (often exponentially; West, 1984) as a function of temperature and if we assume that the interparticle resistance increases as temperature is lowered then one reasonable explanation for the transition is that the higher number of interparticle contacts in the NEI material compared to the ARL material leads to a higher overall resistance. This resistance is not significant at higher temperatures but this resistance becomes more important at low temperature because electronic resistance of semiconductors and insulators is significantly higher at low temperature (West, 1984). At room temperature, another step is rate limiting. Owing to the fact that the smaller particle NEI material has better rate performance at room temperature, we suggest that the room temperature rate is limited by either intraparticle lithium ion diffusion or the number available lithium insertion sites and not interparticle electron transfer. In conclusion, the increased resistance that results from increased interparticle contacts at low temperature seems to be the most reasonable explanation for the transition.

4. CONCLUSIONS

The low temperature performance of nanophase $Li_4Ti_5O_{12}$ as a function of particle size and rate was investigated. Two different $Li_4Ti_5O_{12}$ particle sizes were investigated, 350 and 700 nm, over the temperature range 20, 0, -10, -20, and -30 ºC at low rates (0.1 C, C=theoretical capacity) to high rates (5C). Electrochemical testing revealed that the 350 nm $Li_4Ti_5O_{12}$ material exhibited higher capacity compared to the 700 nm $Li_4Ti_5O_{12}$ at all rates tested at room temperature and at low rates at low temperatures (<0ºC). This expected behavior is a result of the shorter diffusion lengths and higher number of lithium insertion sits in the smaller particle size material. This result reveals the importance of reducing the $Li_4Ti_5O_{12}$ particle size too as small (i.e., from micron to nano) as possible for enhancing low temperature performance. However, at high rates at low temperatures (<0ºC) a change in behavior was observed, in that the larger particle size $Li_4Ti_5O_{12}$ exhibited the higher capacity. It was observed that as the temperature was decreased the rate at which this transition occurred was also lowered. It is believed that the origin of this transition behavior is that as temperature is lowered the resistance of the $Li_4Ti_5O_{12}$ interparticle contacts increases and controls the discharge rate. This result was unexpected and suggests that at low temperatures and high rates just reducing the $Li_4Ti_5O_{12}$ particle size to the nanoscale is not enough to enhance low temperature performance.

The results of this study point out the importance of not only reducing the $Li_4Ti_5O_{12}$ particle size from the micron size to the nanophase size is needed to enhance low temperature performance but, also one must also be concerned with the number and nature of interfaces that are created by use of nanoparticle particles. In order to achieve enhanced low temperature performance at all rates a nanorod architecture (nanometer diameter, micrometer length rods) is preferable to a nanoparticle to minimize interparticle contacts.

ACKNOWLEDGMENTS

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OUTLINE

- Introduction

- Objectives

- Experimental

- Results and Discussion

- Conclusions and Future Directions

INTRODUCTION

• Li-ion batteries are the current/future rechargeable batteries of choice:

Soldier

→ **High Energy**

Hybrid Vehicle
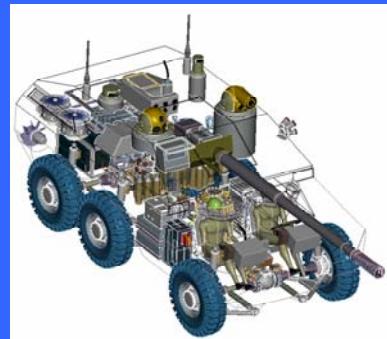
→ **High Power**

MILITARY Li-ION BATTERY CHALLENGES

·Low Temperature Operating Range

    Commercial $\rightarrow$ -20°C

    Military $\rightarrow$ -40°C

OBJECTIVE

Extend the low temperature operating range of Li-ion batteries
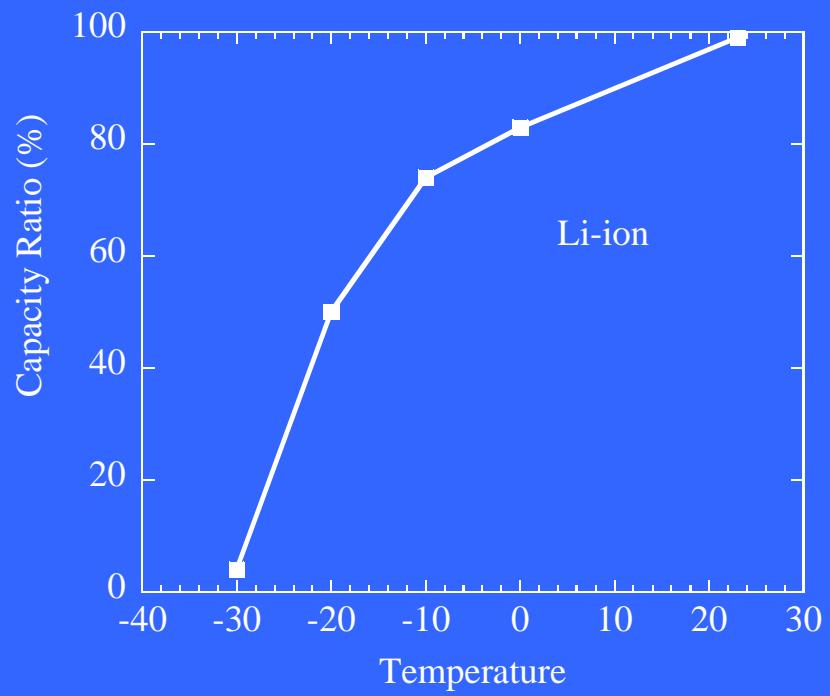
APPROACH

Explore alternative anode materials (i.e., $Li_4Ti_5O_{12}$) to the state-of-art graphite in Li-ion cell

e^- →

| Anode

Graphite

$Li_4Ti_5O_{12}$ | Electrolyte

Li^+ → | Cathode

$LiCoO_2$ |
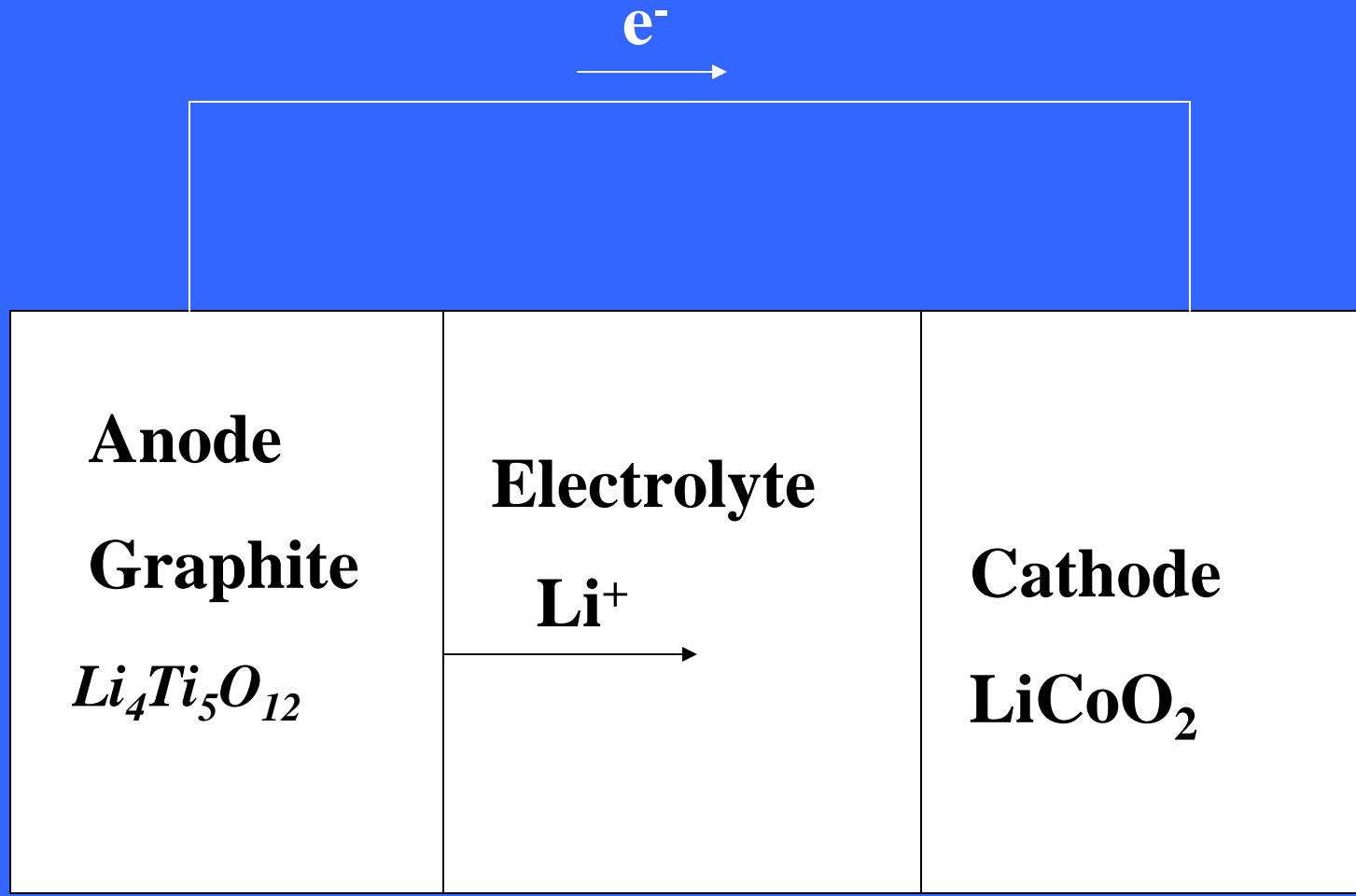
WHY $Li_4Ti_5O_{12}$ INSTEAD of GRAPHITE at LOW TEMPERATURE ???

Main disadvantage of $Li_4Ti_5O_{12}$ vs. graphite

•↓ **energy density ($Li_4Ti_5O_{12}$ ~1.5 V vs. ~0.2 V graphite)**

Advantages of $Li_4Ti_5O_{12}$ vs. graphite

1] No solvent reduction→ No film formation

Lower resistance

No irreversible loss on first few cycles

→Use _nanophase_ particles

2] Well above lithium deposition potential

Recharge at high rates (_military challenge_)

Safe

WHY $Li_4Ti_5O_{12}$ INSTEAD of GRAPHITE at LOW TEMPERATURE

Advantages of $Li_4Ti_5O_{12}$ vs. graphite

3]Zero-strain material

Excellent cycle life

•**As a result of these advantages nanophase $Li_4Ti_5O_{12}$ should make an excellent anode for Li-ion batteries at low temperature**

•**At present no information on the rate capability at low temperature of nanophase $Li_4Ti_5O_{12}$ is available.**

GOAL

•Investigate the low temperature performance of nanophase $Li_4Ti_5O_{12}$ as function of:

1] Particle size
2] Rate

EXPERIMENTAL

- Materials (2 different particle sizes)
  - NEI-$Li_4Ti_5O_{12}$
  - ARL-$Li_4Ti_5O_{12}$ (solid state reaction)

- Characterization (structure and particle size)
  - X-ray diffraction
  - Electron microscopy
 - Surface area measurements (BET)

- Electrochemical Testing (rate capability as function of temperature)
  - Coin cells (Li/electrolyte/$Li_4Ti_5O_{12}$)
 - Temperature range (23°C to -30°C)
 - Rates (0.1 to 5 C, where C=theoretical capacity)

X-RAY DIFFRACTION
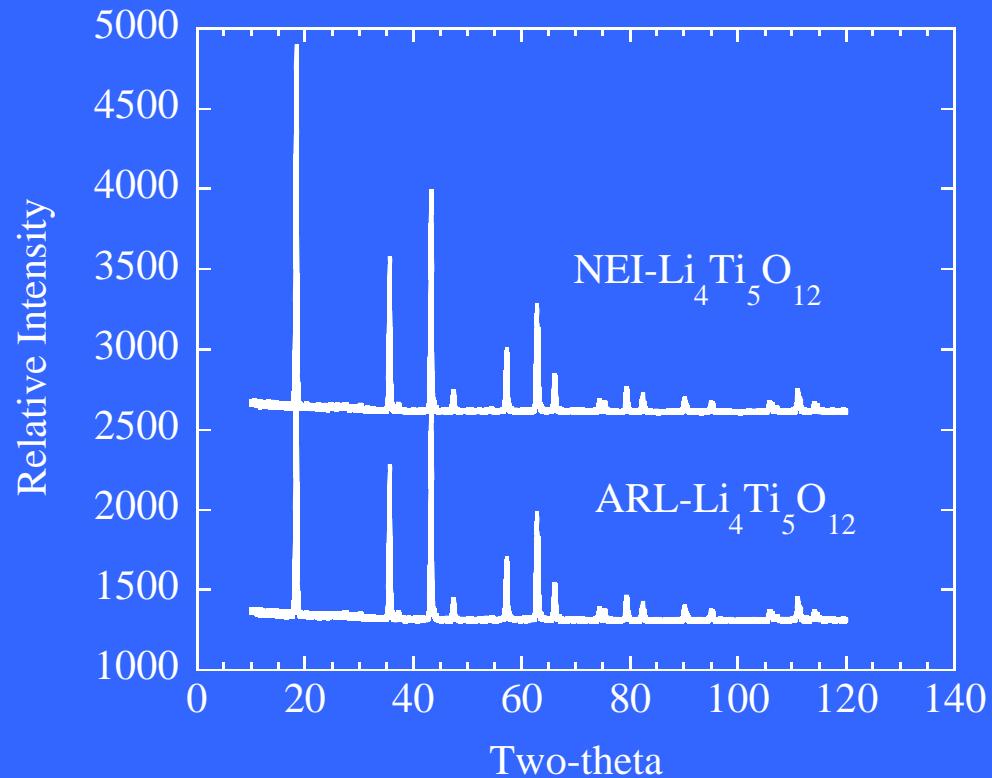
•NEI and ARL Li$_4$Ti$_5$O$_{12}$ → Same structure (spinel)

MICROSCOPY
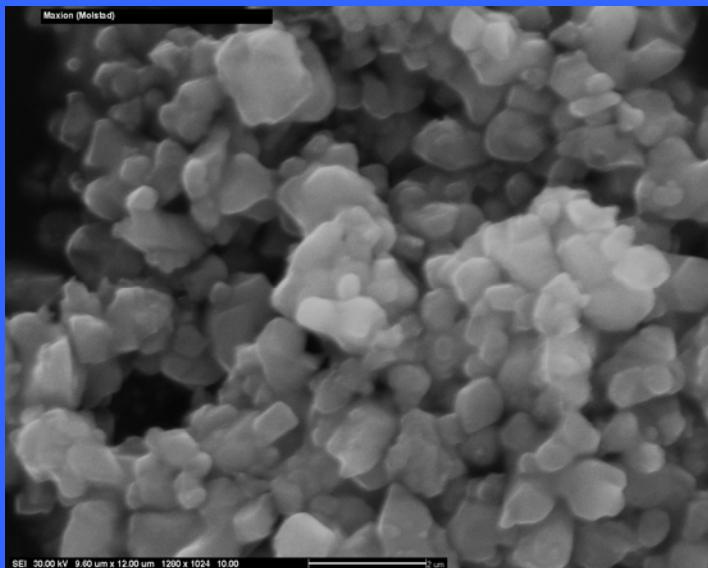
**SEM of ARL-Li$_4$Ti$_5$O$_{12}$
~ 700 nm**
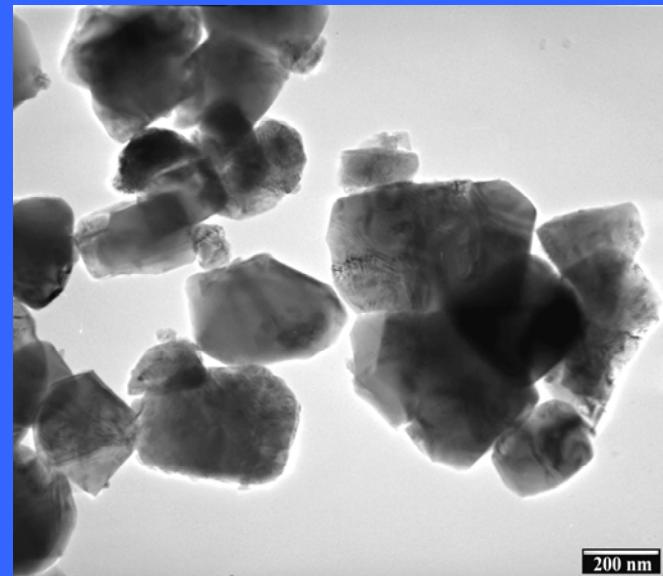
**TEM of NEI-Li$_4$Ti$_5$O$_{12}$
~ 350 nm**

PARTICLE SIZE SUMMARY

Method	ARL-$Li_4Ti_5O_{12}$	NEI-$Li_4Ti_5O_{12}$
SEM	~ 700 nm	-----
TEM	-----	~ 350 nm
BET	~ 700 nm	~ 353 nm

ARL-$Li_4Ti_5O_{12}$ ~ 700 nm vs. NEI-$Li_4Ti_5O_{12}$ ~ 350 nm

ELECTROCHEMISTRY BACKGROUND

A   **B**

$$Li_4Ti_5O_{12} + 3\,Li \rightarrow Li_7Ti_5O_{12} \qquad Capacity = 175\ mAh/g$$

A

Voltage

Discharge Curve

B
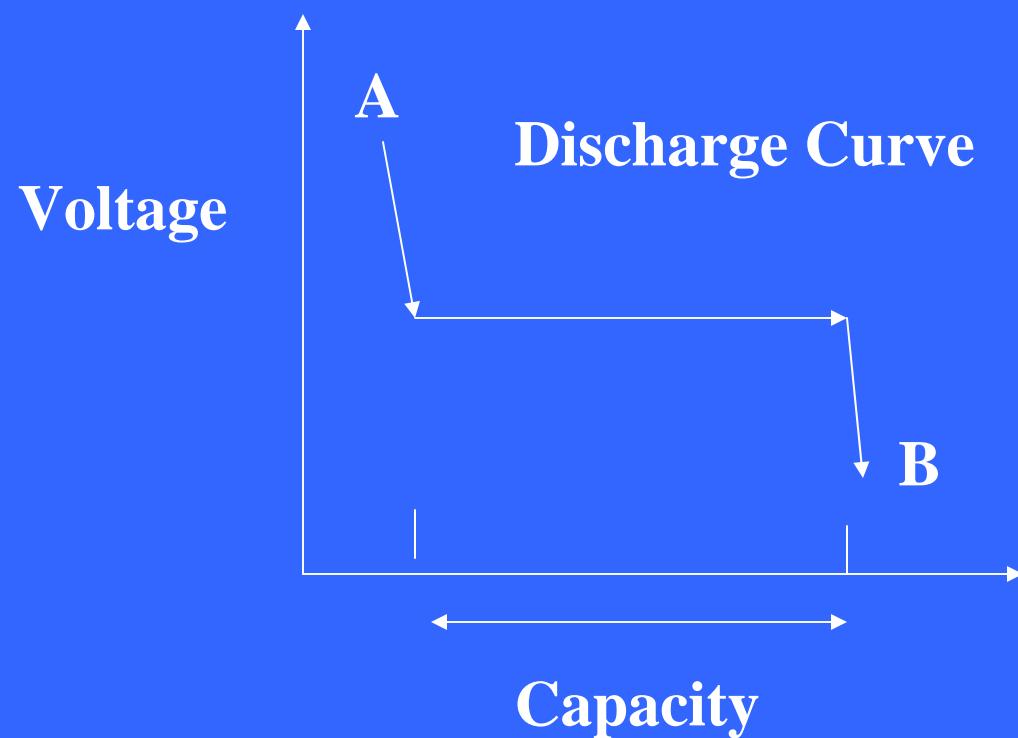
Capacity

EFFECT OF PARTICLE SIZE ON CAPACITY AT 23°C AT LOW RATE
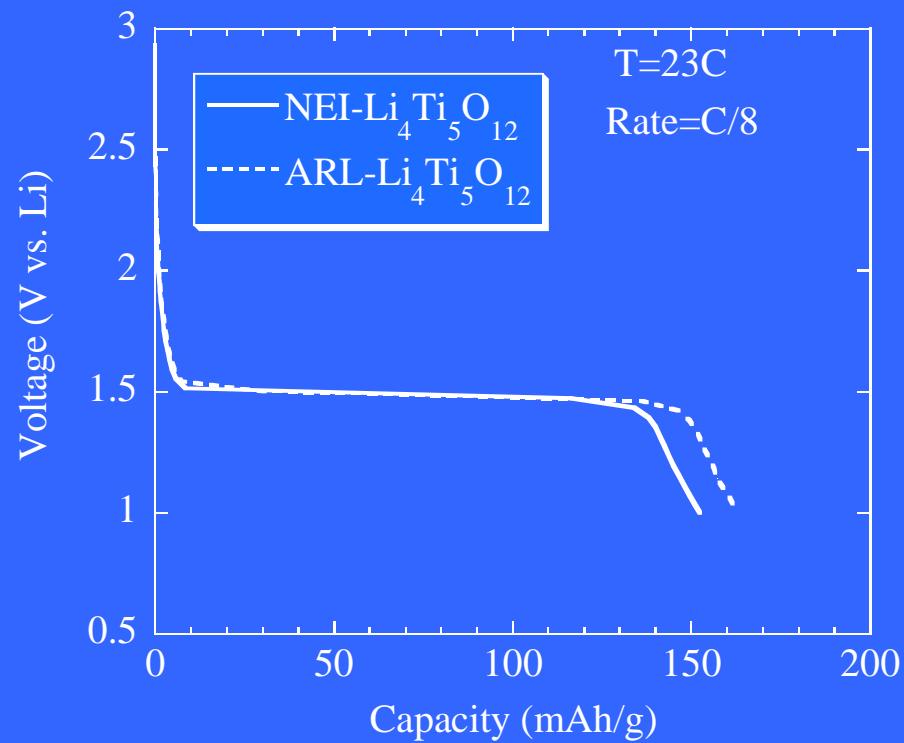
• **23°C ARL-$Li_4Ti_5O_{12}$ and NEI-$Li_4Ti_5O_{12}$ ~same capacity**

EFFECT OF PARTICLE SIZE ON

CAPACITY AT -30°C at LOW RATE
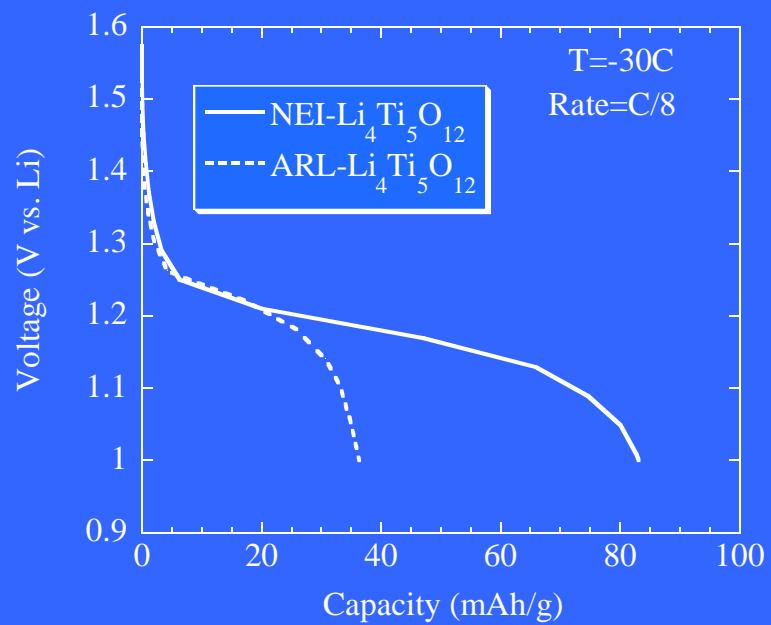
- -30°C NEI-$Li_4Ti_5O_{12}$ >ARL-$Li_4Ti_5O_{12}$ capacity
- Smaller particle size→ reduced diffusion length and increased

  number of Li-ion insertion sites

EFFECT OF RATE ON CAPACITY AT LOW TEMPERATURE
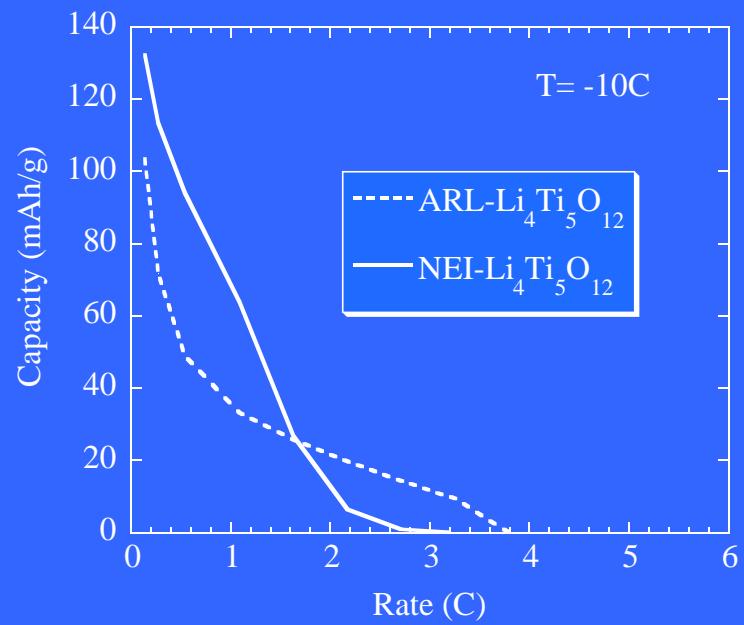
- **As rate is increased the larger particle size has the higher capacity**

TRANSITION RATE AS A FUNCTION OF TEMPERATURE
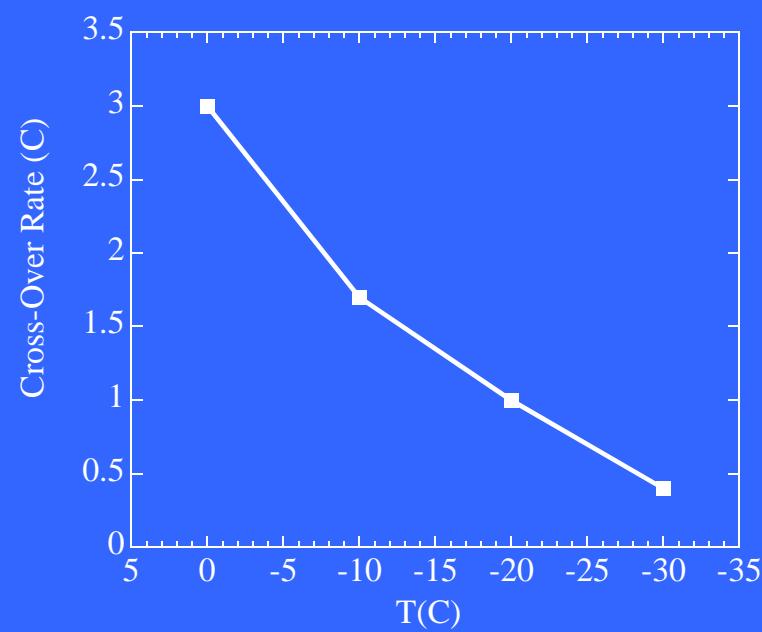
•**Transition rate decreases as temperature decreases**

WHY THE TRANSITION ???

Interparticle resistance becomes rate-controlling
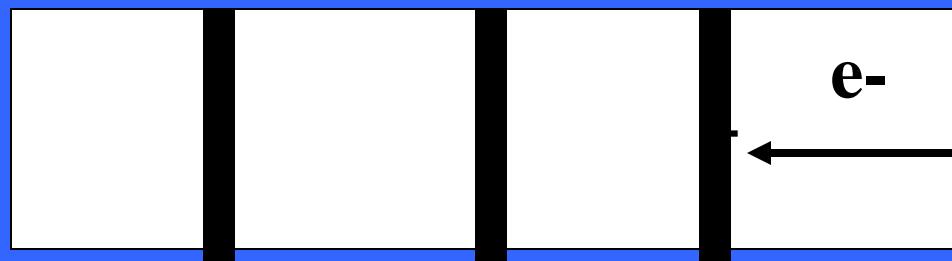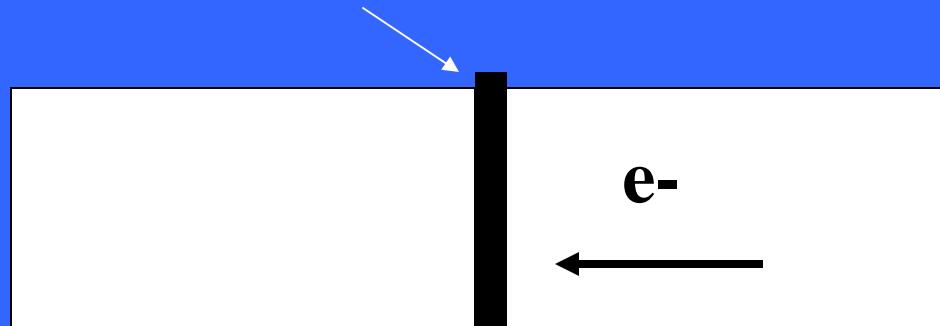
• **Smaller particle size has the larger number of interparticle contacts that become rate-controlling as temperature is lowered**

CONCLUSIONS

1] At low rates and low temperature the smaller particle size $Li_4Ti_5O_{12}$ exhibited higher capacity.

• This is expected as a result of the shorter diffusion length and higher number of insertion sites in the smaller particle size material.

2] At high rates and low temperature the larger particle size $Li_4Ti_5O_{12}$ exhibited higher capacity.

• This is an unexpected and its is believed that as temperature is lowered at high rates it is the interparticle resistance which becomes rate-controlling.

CONCLUSIONS

3] In order to achieve enhanced low temperature performance at all rates a nanorod architecture (nanometer diameter, micrometer length rods) is preferable to a nanoparticle to minimize interparticle contacts.

4] Test nanophase $Li_4Ti_5O_{12}$ with particle sizes less 50 nm

5] Nanophase $Li_4Ti_5O_{12}$ has potential as an anode in Li-ion batteries for use in military applications.